

METHOD FOR COATING A SUBSTRATE

The present invention relates to a method for coating a substrate according to Claim 1, as well as to a coated object according to Claim 8. The preferred field of application is the coating of components for aircraft turbines or gas  
5 turbines, or for garbage incineration plants having temperature-resistant protective layers against high temperature corrosion.

Components for use in aggressive, hot and corrosive conditions  
10 are mostly made of special high temperature alloys based on nickel or cobalt. These alloys are damaged during use, by high temperature corrosion. On account of the high temperatures and accelerated by the presence of even the smallest proportions of chlorine and sulfur, nickel and cobalt  
15 are converted to their oxides and sulfides. The oxides and sulfides of nickel and cobalt are, however, connected only loosely to the metallic undersurface, and scale off little by little.

20 It is known that nickel and cobalt alloys, beginning from a certain proportion of aluminum content, have an increased stability against high temperature corrosion. At high temperatures, these alloys develop on their surface a strongly adherent layer of aluminum oxide which regenerates by itself  
25 if the layer is damaged. In order to be able to select the base material according to strength criteria, methods for diffusion coating were developed, such as alitizing, by which the base alloy may be enriched retroactively with aluminum in the region near the surface.

30 An aluminization method is known from US 3,102,044, in which a layer of aluminum is deposited on the component part. During

the subsequent heat treatment, the aluminum melts and reacts with the substrate to form NiAl.

EP 0 748 394 B1 describes an aluminide coating, enriched with platinum, that is modified with silicon. In order to prepare this layer, in a first step, platinum is deposited on the surface of a nickel superalloy. Subsequently, an aqueous suspension of pulverized elementary aluminum and silicon is applied and dried. Finally the aluminum is molten, whereupon the silicon dissolves and aluminum atoms and silicon atoms diffuse into the substrate.

Another protective layer against high temperature corrosion is made of MCrAlY (M = Ni, Co; CrAlY = chromium aluminum yttrium).

German Patent DE 35 35 548 C2 describes a method for preparing a an MCrAlY coating. By galvanic dispersion deposition, a metal matrix is produced of Ni or Co having intercalated particles made of CrAlY. Upon subsequent tempering, the actual protective layer is then created.

The present invention is based on the object of simplifying known methods for producing temperature-resistant protective layers based on aluminum-containing nickel, cobalt and/or platinum layers, and of making available an alternative protective layer against high temperature corrosion.

This object is attained by the features of the independent claims. Advantageous further developments of the method according to the present invention are described in the dependent claims.

The subject matter of the present invention is a method for coating a substrate, in which, in a first step, nickel, cobalt

and/or platinum are deposited on a substrate in a deposition bath, known as such, without using an external current or electrolytically. In the deposition bath, particles are additionally suspended which contain at least one metal selected from magnesium, aluminum, titanium, zinc, the particles becoming occluded in the coating. Preferably, but not necessarily, the particles do not include any chromium. In the second step, the actual protective layer against high temperature corrosion is produced by heat treatment.

In the method according to the present invention, the reduction of metal salts may take place electrolytically (i.e. by applying an outer current source, or without an external current, that is, by the addition of chemical reducing agents.

In the electrolytic deposition, no chemical reducing agents or their reaction products or decomposition products are present in the deposition bath, that can be inserted into the metal layer that is created and that can contaminate it. If, for example, phosphorus-containing compounds are incorporated, phosphides are created during the heat treatment which make the layer brittle, and thereby sensitive.

The higher deposition speed as compared to the reduction without external current is also advantageous.

In the case of greatly angular component parts, by deposition using chemical reducing agents, one may achieve the formation of a layer having uniform thickness even at the edges and other surface transition points. In such cases, electrolytic deposition supplies nonuniform layer thicknesses, since the electric field is nonhomogeneous because of shadowing processes.

Besides the usual component parts for an external current-free or electrolytic deposition, particles are suspended in the deposition baths of the method according to the present invention, which contain at least one metal selected from magnesium, aluminum, titanium, zinc, and which are inserted into the metal layer being created.

A spatially uniform insertion of the particles is achieved by a homogeneous distribution of the suspended particles in the deposition bath, which may be ensured by various measures, such as stirring, shaking or the application of ultrasound. Because of the spatially uniform insertion of the particles, it is possible to produce a layer having homogeneous properties. Devices and methods which may be used for this are described, for instance, in GB 1 347 184 A and GB 2 014 189 B.

In the second method step, the coated substrate undergoes heat treatment, preferably at 600 to 800° C. During this treatment an alloy forms which contains the elements of the external current-free or electrolytically deposited layer and the elements from the particles. In addition, the atoms diffuse from the deposited layer and the particles into the substrate surface, which results in a better adherence of the layer to the substrate.

The quantity ratios of the deposited metals and particles are preferably chosen in such a way that stable phases are created. If these ratios are not right, a heterogeneous two-phase mixture forms from an alloy-phase and a pure phase. This mixture demonstrates a somewhat worse resistance to hot gases, since it is attacked by intercrystalline corrosion.

If aluminum-containing particles are used, the heat-treated protective layer contains platinum, nickel aluminide and/or

cobalt aluminide which, under high temperature conditions and in the presence of oxygen, forms aluminum oxide layers that stick to the surface and are resistant to corrosion. The presence of noble metals, such as platinum, in the diffusion layer gives rise to the formation of an oxide layer that is almost fault-free. Aluminum may also be totally or partially replaced by magnesium, titanium or zinc. These metals have the advantageous property that they form well-adhering oxide layers at high temperatures, in the presence of oxygen.

The method according to the present invention may be carried out rapidly, simply and using little expenditure in equipment technology, because the necessary elements, which are required for the formation of the protective layer, are able to be applied to the substrate in one working step.

The protective layer produced by the method according to the present invention turns out to be so flat that the surface has to be touched up very little or not at all. A smooth, aerodynamically favorable surface is very important for turbine parts, in order to achieve great efficiency.

In one preferred specific embodiment of the method according to the present invention, particles are used that are made of a single elementary metal.

Elementary, in the sense of the method according to the present invention, means that the particles used may also have a thin oxide layer which, because of the non-noble character of magnesium, aluminum, titanium and zinc are created spontaneously under normal environmental conditions, but no additionally applied oxide layer and no additional components.

These particles are simple and cost-effective to produce, using known instructions.

In one preferred specific embodiment of the method according to the present invention, particles are put in that have an oxide layer which is thicker than the oxide layer formed under normal environmental conditions.

An oxide layer having the thickness mentioned brings on a greatly improved chemical stability of the particles in acid and basic deposition baths, especially in the pH range between 4 and 9. The deposition baths used may therefore be used longer before having to be changed.

Besides, the use of these chemically more stable particles does not limit the choice of the deposition bath used, since that deposition bath may be selected which supplies the metal layers having the best properties, and the deposition bath does not have to be selected according to whether the particles used in it are stable.

Magnesium, aluminum, titanium and zinc are non-noble metals which are not stable under acid conditions, but which dissolve as metal ions. Aluminum and zinc also dissolve under basic conditions because of their amphoteric character, as aluminate or zincate. The solution of the particle in the deposition bath has the effect that interfering foreign substances gradually accumulate in the bath. The baths set for the purpose of an optimal deposition result are toxified in a creeping manner. As a result, the efficiency of deposition becomes worse. In addition, layers that are more and more porous are formed, since the increasing development of hydrogen interferes with the formation of a smooth, uniform layer of high density.

Preferably, the oxide layer is at least twice as thick as the oxide layers that magnesium particles, aluminum particles,

titanium particles and zinc particles form spontaneously under normal environmental conditions.

Investigations have shown that magnesium particles, aluminum particles and zinc particles having an oxide layer of at least 0.3  $\mu\text{m}$  in thickness have an especially good chemical stability.

Known methods for producing the oxide layer may be employed. The simplest method is the reaction of the metal particles with hot water. In order to improve the thickness and the density of the oxide layer, inhibiting or complexing additives may be used. Examples are carbonates, silicates and phosphates. Oxidizing agents such as persulfate compounds or chromates may also increase the thickness and the density of the oxide layer. Aluminum particles are preferably provided with an oxide layer according to the Alrok method, in which sodium carbonate and potassium dichromate are used, or according to the Erftwerk method, in which sodium carbonate, sodium chromate and sodium silicate are used.

The layer thickness of the oxide skin should be thin enough that the particle receives a sufficient proportion of elementary metal, so that the subsequent formation of an alloy with nickel, cobalt or platinum is not interfered with.

In one preferred specific embodiment of the method according to the present invention, magnesium particles, aluminum particles, titanium particles and/or zinc particles are used that are alloyed with nickel, cobalt and/or platinum.

These particles have the advantage that they are relatively stable in acid and basic deposition baths having a pH value between 3 and 10. As was explained above, one may therefore choose between a greater number of deposition baths.

Furthermore, in this way additional components may be introduced for the subsequent alloy formation in the tempering process. This makes possible a still greater freedom of choice in the selection of the deposition bath, since the conditions have to be optimized only for the deposition of a metal.

In one preferred specific embodiment of the method according to the present invention, silicon particles are additionally suspended in the deposition bath, which become occluded in the coating.

The heat-treated, silicon-modified layer is more ductile than layers without silicon, and therefore demonstrates a lower tendency to crack formation.

Silicon may also be introduced into the coating by using magnesium particles, aluminum particles, titanium particles and/or zinc particles that are alloyed with silicon.

Besides the quantities used, the ratio in which the particles are inserted into the layer is a function of additional parameters, such as the speed of settling in the deposition bath. In the case of particles that contain alloys, this quantity ratio is established ahead of time. Thereby, the problem arising in connection with using particles made of different materials, namely of a different rate of insertion, is sidestepped. In a further preferred specific embodiment of the method according to the present invention, the layer is deposited up to a thickness of 10 to 100  $\mu\text{m}$ , preferably 30 to 70  $\mu\text{m}$ .

Experiments have shown that layers produced using the method according to the present invention, especially those having a



thickness of 10 to 100  $\mu\text{m}$ , have excellent corrosion resistance.

In one preferred specific embodiment of the method according to the present invention, particles having a diameter of 1 to 50  $\mu\text{m}$ , preferably 5 to 20  $\mu\text{m}$ , are used.

Particles of this size may be suspended in homogeneous distribution in the deposition bath. This fulfills a prerequisite for a spatially uniform insertion of the particles into the deposited layer.

Particles that are smaller than 1  $\mu\text{m}$  tend to aggregation when in suspension, that is, they form clusters. Bigger particles than 50  $\mu\text{m}$ , even when they are able to be suspended homogeneously, which becomes more and more difficult with increasing size, lead to nonuniform spatial distribution of the particle material in the layer, since they are large compared to the layer that has a thickness of 10 to 100  $\mu\text{m}$ . Basically, magnesium-containing, aluminum-containing and titanium-containing particles, because of their lower density, may be selected to be larger than zinc-containing particles.

The present invention will be explained in greater detail in the light of the following example, without limiting it to this example.

Component parts of a cooling system were coated so as to be resistant to hot gas corrosion. The component parts, which were made up of a Ni-based alloy, were degreased by ultrasound cleaning, were pickled and provided with a 0.5  $\mu\text{m}$  layer made of strike nickel. Using a galvanic Ni electrolyte, which contained particles made of an Al<sub>88</sub>Si<sub>12</sub> alloy having a diameter of 3  $\mu\text{m}$  in a concentration of 10 g/l, a dispersion layer was deposited. At a current density of 500 A/m<sup>2</sup> and

moderate electrolyte motion and component part motion, a layer of a thickness of 30  $\mu\text{m}$  was applied. By REM measurement (REM = *Rasterelektronenmikroskop* (scanning electron microscope)) one was able to show that 25 % by volume of the deposited layer was made up of AlSi particles. There followed a two-hour tempering process at 750° C for the formation of the desired alloy layer.